

The University of Chicago

THE
AUTOCATALYTIC DECOMPOSITION
OF BENZOPHENONEOXIME
IN ACETIC ACID

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
1937

By
JOHN CRYER

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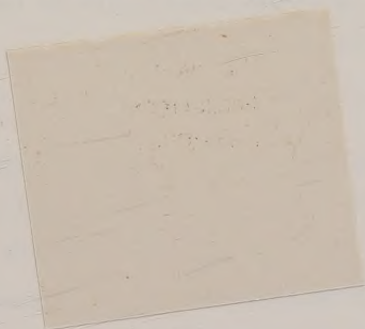
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ACKNOWLEDGMENT

This research was done under the direction of Professor Julius Stieglitz and of his associate, Dr. Raymond W. Johnson. For the absorption spectra measurements I am indebted to the courtesy of Dr. Albert E. Sidwell. Throughout the work I have had the great advantage of the searching and fruitful criticisms of my friend, Mr. Edgar Eisenstaedt.

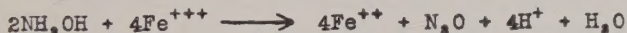


THE AUTOCATALYTIC DECOMPOSITION
OF BENZOPHENONEOXIME
IN ACETIC ACID

In the course of some work which was being done to measure the amount of oxime which had been hydrolyzed in an acetic acid-hydrochloric acid solution of benzophenoneoxime, it was found that benzophenoneoxime underwent a transformation in an acetic acid solution. The oxime was dissolved in acetic acid containing a small amount of water, and, after an induction period of some hours, a reaction occurred in which the concentration of the oxime dropped to zero. An investigation of this phenomenon was the subject of the present research, and it was found that, in acetic acid solutions containing suitable amounts of water, benzophenoneoxime undergoes an autocatalytic decomposition.

The Volumetric Determination of Hydroxylamine

A volumetric method for the quantitative determination of hydroxylamine was described by Meyeringh¹ and improved by Raschig.² It consists in the oxidation of the nitrogen of the hydroxylamine to nitrous oxide by means of ferric salts in hot acidic solution, the equivalent amount of ferrous salt produced being titrated with standard potassium permanganate solution:

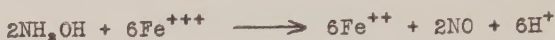


It is important that a considerable excess of ferric salt be em-

¹Meyeringh, Ber. **10**, 1942 (1877).

²Raschig, Ann. **241**, 188 (1887); Z. angew. Chem. **17**, 1411 (1904).

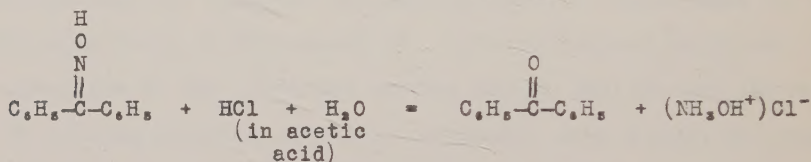
ployed, otherwise some nitric oxide is produced and the analysis is not reliable:



The method has been used subsequently by other investigators,³ and, in particular, was given a careful and thorough examination by Bray, Simpson, and Mackenzie,⁴ who found it to be completely satisfactory.

The Hydrolysis of Benzophenoneoxime

Benzophenoneoxime is hydrolyzed in acid solution to give benzophenone and hydroxylamine:



R. W. Johnson⁵ followed the rate of hydrolysis of benzophenoneoxime, in a solvent consisting of equal parts by volume of acetic acid and 1 N hydrochloric acid, by using the analytical method described in the preceding section to determine the concentration of hydroxylamine in samples withdrawn at intervals of time during the hydrolysis, having first removed the unchanged oxime by extraction with chloroform.

A Volumetric Method for the Determination of an Oxime

The work of these investigators indicated a convenient method for the volumetric estimation of an oxime, namely, the

³Ebler and Schott, J. prakt. Chem. (2) 78, 320 (1908); Sommer and Templin, Ber. 47, 1226 (1914).

⁴Bray, Simpson, and Mackenzie, J. Am. Chem. Soc. 41, 1366 (1919).

⁵Johnson, J. Am. Chem. Soc. 56, 1904 (1934).

dissolution of the oxime in acetic acid, followed by its oxidation by boiling with excess ferric sulphate made strongly acid with sulphuric acid. The ferrous sulphate produced is determined by titration with potassium permanganate.

This analytical method was tested by analyzing benzo-phenoneoxime. The oxime was prepared according to the method of Auwers,⁶ but it was found to be unnecessary to heat the reactants; indeed, the heating is a disadvantage, for the purest product is obtained by allowing the reactants to stand at room temperature for two hours, and no recrystallization is necessary.

Analyses of the oxime prepared in this way were completely satisfactory, provided that certain precautions were taken regarding the acetic acid used as solvent. A convenient test as to the suitability of an acetic acid for the purpose is to determine hydroxylamine itself in the presence of the acid in question. For instance, a sample of hydroxylamine hydrochloride is weighed out and analyzed in aqueous solution by the method referred to at the beginning of this paper; a similar analysis is then made with the acetic acid present: if the two analytical results are sufficiently close, the acid is satisfactory.

The Determination of Hydroxylamine in the Presence of Acetic Acid

A number of different acetic acids were tested in this way, and they proved unsatisfactory. The difficulty of obtaining pure acetic acid has been mentioned by several workers,⁷ and the disagreement which is to be found in the literature as to the values of the physical constants of this acid is evidence of the fact; moreover, in the present instance, a surprisingly large

⁶Auwers, Ber. **22**, 604 (1889).

⁷Ramsay and Young, J. Chem. Soc., **49**, 791 (1886)

variation in an analytical result appeared to arise from what might be considered an almost negligible difference in the acid.

Five analyses, in aqueous solution, of a sample of hydroxylamine hydrochloride gave values varying between 99.06 % and 99.33 % (average, 99.24 %). This figure was confirmed by titrating the hydroxylamine hydrochloride against standard potassium hydroxide, using phenolphthalein indicator:⁸ five analyses by this method gave values varying between 99.10 % and 99.31 % (average, 99.21 %). It was considered as established, therefore, that the analytical purity of the hydroxylamine hydrochloride used was 99.23 % $\pm$ 0.03. When the hydroxylamine hydrochloride was determined by carrying out the oxidation in a similar way, except that 25 cc. of acetic acid had been added, a great variation in results appeared. Two analyses in the presence of an acetic acid supplied by General Chemical Company, labelled "U. S. P.", gave values of 101.4 %: Merck's acetic acid, labelled "Reagent Grade", gave 102.6 % and 103.1 %; doubling the weight of the sample of hydroxylamine hydrochloride, this acid gave 101.9 %, while, with a sample of one-third the weight, it gave 104.9 %: Mallinckrodt's acetic acid, labelled "C. P.", gave 100.8 % and 100.6 %: Kahlbaum's 100 % acetic acid, labelled "zur Analyse", gave 99.28 % and 99.04 %. These differences must be caused by some reaction between the dissolved hydroxylamine hydrochloride and impurities in the acetic acid used, for the blank analyses on three of the acids differ by an insignificant amount (0.01 cc. of permanganate); and in the case of the Mallinckrodt "C. P." acid, for which the blank analysis differs more widely (0.07 cc. of permanganate), the values obtained

⁸Treadwell and Hall, "Analytical Chemistry", John Wiley and Sons, New York, 1930, p. 498.

for the hydroxylamine hydrochloride analysis are more nearly in accord with the correct figure. The pair of analyses, obtained in the presence of Kahlbaum's 100 % acid, show that it is possible to obtain an acid of sufficient degree of purity for the purpose.

The Purification of Acetic Acid

Attempts were made to purify the General Chemical Company's "U. S. P." acid by fractional distillation. For this purpose a Snyder⁹ column, equipped with a suitable dephlegmator, was employed. This column effects a complete separation of water from acetic acid, and it was found to be a much more convenient means of doing so than the fractional crystallization methods which have generally been employed for this purpose.¹⁰

The "U. S. P." acid was separated into five fractions, and these fractions, in order of increasing boiling points, affected the analysis of hydroxylamine hydrochloride in the following way: 102.1 %; 100.8 %; 99.4 %; 99.7 %; 98.1 %. Fractionation of a sample of Mallinckrodt's "C. P." acid gave similar results.

Attempts to obtain a suitable acid by fractional crystallization were also unsuccessful: for example, one crystallization of Mallinckrodt's "C. P." acid changed the value obtained in the hydroxylamine hydrochloride analysis test from 100.7 % to 99.6 %; a second crystallization left this value unchanged.

It was thought that the objectionable impurities might be removed by refluxing the acid with hydroxylamine hydrochloride,

⁹Hill and Ferris, Ind. Eng. Chem. **19**, 379 (1927).

¹⁰Rüdorff, Ber., **3**, 390 (1870); Ramsay and Young, op. cit.; de Visser, Rec. trav. chim., **12**, 118 (1893); Bousfield and Lowry, J. Chem. Soc., **99**, 1436 (1911).

and subsequently distilling it. This was tried with Merck's "Reagent Grade" acid, but the value in the hydroxylamine hydrochloride analysis was unchanged; originally 102.1 %, after the process it was found to be 102.3 %.

Distillation of Merck's "Reagent Grade" acid from potassium dichromate and sulphuric acid seemed to result in a great improvement, the degree of improvement depending upon the relative amounts of dichromate and acid used: using the proportions that were found to be most suitable, Mallinckrodt's "C. P." acid was treated in this way, and an acid was obtained which, when tested by the hydroxylamine hydrochloride analysis, gave the values 99.2 % and 99.3 %. However, the analytical figure obtained appeared to depend upon the weight of hydroxylamine hydrochloride used, for, when the amount was doubled, the value became 99.9 %, and when the amount was reduced to one-third, it became 98.4 %.

Distillation of Mallinckrodt's "C. P." acid from potassium permanganate actually made the analyses worse.

Another acetic acid was obtained by distillation from a mixture of Na acetate (Mallinckrodt, labelled "Pure, Anhydrous") and concentrated sulphuric acid. The acid produced was distilled carefully from barium acetate, and fractionated by means of the Snyder column. The hydroxylamine hydrochloride analysis made in the presence of this acid, gave a value 98.7 %; with double the amount of hydrochloride, the value 99.1 % was obtained, and with one-third the amount, 96.3 %.

A completely satisfactory acid was found in the synthetic acetic acid supplied by the Niacet Chemicals Corporation of Niagara Falls. This acid contains only 0.10 % water as it comes from the factory in carboy lots. Hydroxylamine hydrochloride analyses, made in the presence of this acid, gave the following

figures: 99.33 % and 99.26 % ; with double the amount of hydrochloride, the figure was 99.33 % , and with one-third the amount, 99.28 % . After fractionation through the Snyder column, an anhydrous acid was obtained, and for this the hydroxylamine hydrochloride analysis gave the value 99.17 % ; with double the amount of hydrochloride it was 99.42 % , and with one-third the amount, 99.34 % . From the point of view of this analysis, therefore, the acid is quite satisfactory as it comes from the carboy. In the course of the work, however, a sample had been carefully fractionated by use of the Snyder column, and the employment of this anhydrous acid led to interesting results later.

Values of Some Physical Constants for Acetic Acid

The anhydrous acid melts at 16.70°, ¹¹ and boils at 118.3°. ¹² its density at 25°, relative to water at 4°, is 1.044. ¹³ The most rapid method of determining the water content of any particular sample of acetic acid is by the freezing point, and, for small amounts of water, it is by far the best. The variation of the freezing point with dilution has been determined by a number of different workers, and their results are in very good agreement except in the region 99.8 % - 100.0 % : here, in general, the values wander and seem to be low; in particular, the value 16.60°, for the freezing point of 100.00 % acid, is not in agreement with the general direction of the freezing-point curve.

¹¹Rüchdorff, op. cit.; de Coppet, Ann. chim., (7), 16, 275 (1899); 18, 142 (1899); Dahms, Ann. chim., (7), 18, 140 (1899); de Visser, op. cit.; Bousfield and Lowry, op. cit.; Craven and Kershaw, J. Soc. Chem. Ind., 56, 72 (1937).

¹²Ramsay and Young, op. cit.; Kahlbaum, Z. physik. Chem., 26, 591 (1898); Bousfield and Lowry, op. cit.

¹³Ramsay and Young, op. cit.

Rüdorff¹⁴ records the value 16.70°, and this agrees with the value obtained in the course of the present research. A freezing-point graph (Fig. 1) was plotted for the values recorded by Rüdorff,¹⁵ de Coppet,¹⁶ Dahms,¹⁷ and the Niacet Chemicals Corporation,¹⁸ and this was used in the determination of the composition of the acetic acids used in the work described.

The Absorption Spectrum of Acetic Acid

Since it was evident that the impurities, which gave rise to the difficulties in the analysis for hydroxylamine, were present in only exceedingly small amounts, absorption spectra measurements for three of the acids were made. These were done with the photoelectric spectrophotometer.¹⁹ The three acids used were 100.00 % Niacet acid, Kahlbaum's 100 % acid, labelled "zur Analyse", and Merck's acid, labelled "Reagent Grade"; the percentage of light transmitted, as compared with that transmitted by water, was measured for each, and graphs were plotted (Fig. 2). Over the entire region of wave lengths employed, the Niacet acid shows the least absorption, and is, therefore, to be considered the purest.

The Analysis of Benzophenoneoxime in Acetic Acid Solution

The 100.00 % Niacet acetic acid was used in the analysis of benzophenoneoxime with satisfactory results. Pairs of analyses on five different preparations of this oxime gave the following values for the percentage of nitrogen in the oxime: 7.18 %

¹⁴Rüdorff, op. cit. ¹⁵Ibid. ¹⁶de Coppet, op. cit.

¹⁷Dahms, op. cit.

¹⁸Leaflet distributed by Niacet Chemicals Corporation.

¹⁹Hogness, Zscheile, and Sidwell, J. Phys. Chem., **41**, 379 (1937).

FREEZING POINT OF AQUEOUS SOLUTIONS OF ACETIC ACID

F.P. (°C.)

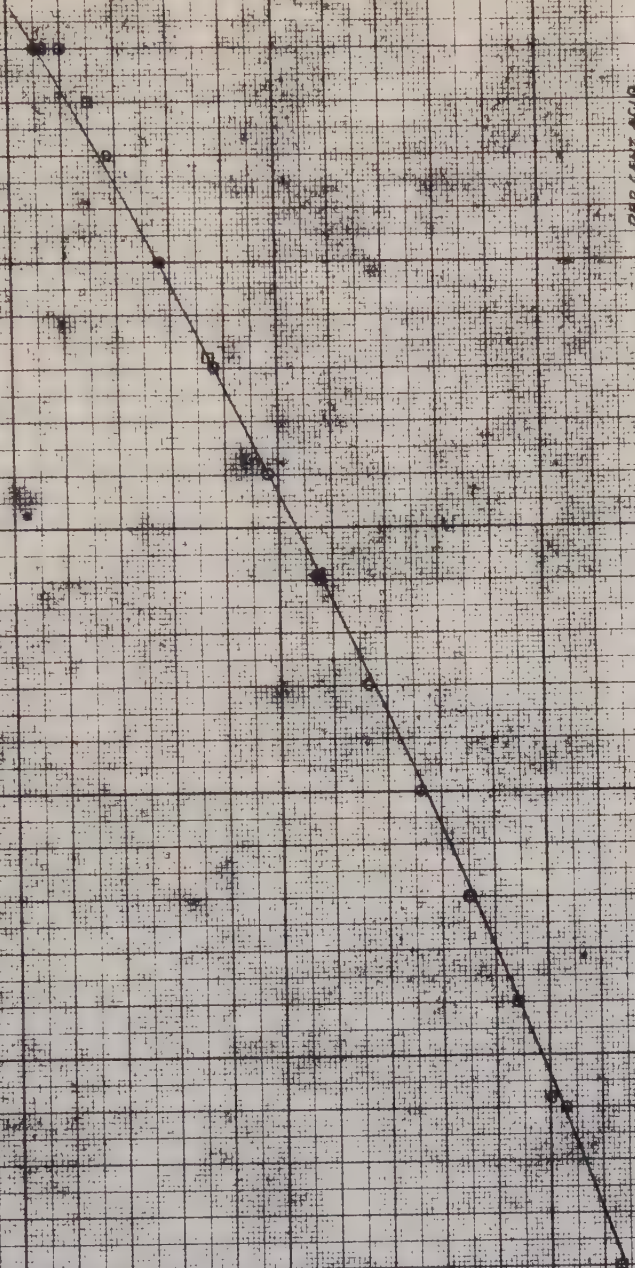
○ MIXER CHEMICALS CORPORATION

□ DOW
▲ RUOFF
x de CORNET

PERCENT ACID

17.0
16.8
16.6
16.4
16.2
16.0
15.8
15.6
15.4
15.2
15.0
14.8
14.6
14.4
98.8

98.8 98.9 99.0 99.1 99.2 99.3 99.4 99.5 99.6 99.7 99.8 99.9 100.0



and 7.18 %; 7.16 % and 7.17 %; 7.12 % and 7.11 %; 7.08 % and 7.12 %; 7.08 % and 7.07 %. The calculated value is 7.11 %.

This method was tested further by making analyses of a different oxime, namely, p,p'-dimethoxybenzophenoneoxime. Pairs of analyses on three different preparations of this oxime gave the following values for the percentage of nitrogen: 5.50 % and 5.48 %; 5.51 % and 5.51 %; 5.50 % and 5.52 %. The calculated value is 5.45 %.

The Decomposition of Benzophenoneoxime

The oximes are not specially stable substances, and, under ordinary laboratory conditions, they often decompose on standing. Benzophenoneoxime readily undergoes a transformation into a variety of products, if left standing in the laboratory for a few days. After the transformation has occurred, the dish which contained the oxime is found to contain a brownish oil. The interval of time which elapses before the change occurs - the induction period - depends upon conditions, but once the change is initiated it takes place rapidly. This period is shorter if the oxime is stored in a closed vessel containing the ordinary atmosphere of a chemical laboratory - for example, a desiccator - than it is if the oxime is allowed to stand in the open. The oxides of nitrogen* are especially active in promoting the change, and, if the oxime is placed in a closed desiccator in which the transformation of a previous sample has already taken place, the induction period is very short; under these circumstances, a freshly-prepared oxime may be completely transformed in a few hours: on

*Throughout this paper the phrase "the oxides of nitrogen" denotes the gases present when nitric oxide and oxygen are mixed, namely the oxides with the formulae, NO, NO₂, N₂O₄, N₂O₅.

the other hand, if the desiccator is made scrupulously clean, and is filled with air uncontaminated with laboratory gases, or is evacuated, a freshly-prepared sample of benzophenoneoxime may be stored in it for weeks without decomposition. When the oxime decomposes in air, oxygen is absorbed;²⁰ if, for example, the decomposition occurs in a closed desiccator containing air at atmospheric pressure, the residual gases in the desiccator after the decomposition are at a pressure much lower than one atmosphere. If it is desired to preserve an oxime, the main thing seems to be to avoid all access of the oxides of nitrogen. Benzophenoneoxime may be stored indefinitely in an atmosphere of air, of carbon dioxide, of oxygen, of nitrous oxide, or of nitric oxide; but in the presence of the oxides of nitrogen decomposition is rapid.

The decomposition of benzophenoneoxime has been studied by several investigators.²¹ Various products of the decomposition have been observed; for example, benzophenone, iminodiphenylmethane, toluene, nitrotoluene, benzene, nitrobenzene, nitrogen, oxides of nitrogen, ammonia, nitric acid and water.

The Change in Concentration of Benzophenoneoxime in Acetic Acid

When dissolved in 100.00 % acetic acid, freshly-prepared benzophenoneoxime appears to remain unchanged indefinitely; analysis of the solution for oxime, in the manner described above gives an analytical figure that is slightly too high, the apparent increase in the concentration of the oxime occurring almost immediately on dissolution, and then remaining unchanged. In 99.84 % acetic acid, however, analysis shows the slight increase

²⁰Hollemann, Rec. trav. chim., **13**, 429 (1894).

²¹Hollemann, op. cit.; Konowalow, Chem. Zentr., **I**. (1906), 72; Lachman, J. Am. Chem. Soc., **46**, 1473 (1924).

which appeared in the case of the 100.00 % acid, followed by a period of some three to six hours over which the analytical value remains constant; but then a decrease in value occurs, and at a rapidly accelerating rate, until, finally, the amount of oxime found analytically has dropped to somewhere near the value zero. The change is an autocatalytic one, and it is natural to suppose that it is related to the change which occurs when solid benzo-phenoneoxime decomposes in the manner already described.

The method of analysis, which has been discussed, provides a convenient way of following the decline in concentration of the oxime. Such measurements were made, and graphs constructed from the values obtained (Figs. 3 and 4). In 99.50 % acetic acid this transformation does not occur, the behaviour of this acid, in so far as the analytical determination of the oxime is concerned, being similar to that of the 100.00 % acid.

The transformation thus appears to occur only when the oxime is dissolved in acetic acid of composition intermediate to 99.50 % and 100.00 % . This statement is true only for the freshly-prepared oxime, or for an oxime in which incipient decomposition is not already established. When the initial stage of decomposition has already been reached, the transformation of the oxime proceeds, even in 100.00 % acetic acid, or in 98 % acid. But, quite often, a transformation which occurs under these conditions is not complete, and, after proceeding part way, the concentration of the oxime remains constant at some value lower than the initial one. Furthermore, a very slight variation in the water content of the solvent acid affects the course of the transformation; a freshly-prepared oxime, dissolved in an acid in which the water content is not exactly favourable, after going through an induction period, and then through the initial stages

of decomposition, may come to a constant state, before the transformation is completed, at any concentration between the initial value and zero.

The measurements described in the experimental part of this paper were all made using the 100.00 % Niacet acetic acid, or an acid derived from it by adding the requisite amount of water; but the transformation of benzophenoneoxime in acetic acid solution is not confined to this particular acid; Mallinckrodt's "C. P." acetic acid, when fractionated, and the fraction of suitable composition (99.84 %) chosen, gave the transformation also.

The Change in Concentration of Nitrite Ion in Acetic Acid Solutions of Benzophenoneoxime

Concurrently with the change in concentration of the oxime in acetic acid solution, there occurs a change in the concentration of nitrite ion. This change can be followed readily by a colorimetric method²² which involves treating the solution with α -naphthylamine and amino G-salt. Indeed, this colour test is of great value in indicating when the induction period in any particular case is at an end: for, at the time of the dissolution of the oxime in the acetic acid, the nitrite ion test will be negative; but, as the induction period ends, and before any change in the concentration of the oxime can be detected by the analytical method employed, a faint positive colour test for nitrite ion will be in evidence. Colorimetric measurements showed that, after the end of the induction period, the concentration of nitrite ion increased rapidly to a maximum, then fell

²²Stieglitz and Palmer, J. Pharmacol. Exper. Therap., 51, 398 (1934).

away somewhat less rapidly until most of the oxime had been transformed, and then very gradually faded away to lower and lower values.

The Catalytic Effect of Certain Substances on these Changes

The presence of small amounts of certain substances markedly shortens the induction period of this reaction. For example, sodium nitrite, when present at a concentration of 0.00005 g. per 100 cc., shortened the induction period by some 95 %; nitrous oxide, when present at a concentration of 0.0001 g. per 100 cc., shortened the induction period by about 72 %, and when present at a concentration of 0.00005 g. per 100 cc., shortened the induction period by about 33 %. For a freshly-prepared oxime, dissolved in 100.00 % acid, the addition of even relatively large amounts of sodium nitrite, of nitrous oxide, of nitric oxide, or even of the oxides of nitrogen, does not cause the transformation to take place.

The nitrous oxide used for this part of the work was prepared as described in the experimental section, and, since the oxides of nitrogen are very active in promoting the transformation of benzophenoneoxime, it was especially important that the nitrous oxide should not be contaminated with them. The method used to secure purity in this respect, was to pass the gas in an exceedingly fine stream and very slowly through a Milligan wash-bottle containing a solution of potassium hydroxide, and then through a second Milligan wash-bottle containing a solution of α -naphthylamine and amino G-salt. The nitrite ion test, described in the preceding section, is stated to be sensitive to one part in seven hundred and fifty million.²³ The reaction in-

²³Stieglitz and Palmer, op. cit.

volved in the test, therefore, should be a very efficient one for removing the last traces of the oxides of nitrogen. A method of purification such as this should be a general one; any very sensitive test for a substance might depend upon a reaction that could be employed in such a way as to remove small traces of that substance from another which is contaminated by it. Before any nitrous oxide was collected for use in the catalytic study, a test showed that it was free from the oxides of nitrogen so far as the Stieglitz-Palmer²⁴ modification of the Ilosvay²⁵ test is concerned. Of course, there is always the possibility that the catalytic effect noted in the case of nitrous oxide was due to the presence of an amount of the oxides of nitrogen so small that it was undetected by the colour test used.

Since the change possesses characteristics which suggest the phenomenon of auto-oxidation, and since one important school of thought on that subject holds the view that the initial step in any auto-oxidation involves the formation of a peroxide, and since, further, acetanilide is used as a preservative in hydrogen peroxide, it was thought that acetanilide might inhibit the progress of the transformation of the oxime. But experiment showed that the presence of acetanilide, up to a concentration of 0.0003 g. per 100 cc., was without effect on the induction period of the reaction.

Relationship between the Changes in Concentration of Oxime and of Nitrite Ion

Two sets of experimental measurements were made in which both the change in the concentration of the oxime and the change

²⁴Stieglitz and Palmer, op. cit.

²⁵Ilosvay, Bull. soc. chim., 2, 347 (1839).

in the concentration of the nitrite ion were measured for the same solution. Both experiments indicated that the nitrite ion has its maximum concentration in the solution at about the same time that the rate of change of the oxime concentration is at its maximum.

Experimental Part

The Preparation of Benzophenoneoxime

The method used is a modification of that described by Auwers.²⁶ A 5.00 g. sample of benzophenone (Eastman, m.p. 48.3°) was dissolved in 100 cc. 95 % ethyl alcohol. To this solution the following two solutions were added: first, 6.0 g. hydroxylamine hydrochloride dissolved in 20 cc. water; second, 14.0 g. potassium hydroxide dissolved in 20 cc. water. The flask containing the reactants was covered with a piece of filter paper and allowed to stand at room temperature for two hours, with occasional shaking. At the end of that time, the contents of the flask were poured into 200 cc. cold water, and, after standing for a few minutes, this liquid was filtered, with suction, through a sintered glass filter to remove particles of dirt and any unchanged benzophenone. The filtrate was poured into 2 1/2 litres of cold water, and 15 cc. glacial acetic acid was added, very slowly and with constant stirring. The precipitated oxime was collected on a sintered glass filter, washed thoroughly with a copious supply of cold water, and then placed in a vacuum desic-

²⁶Auwers, op. cit.

cator, over phosphorus pentoxide, to dry. The yield of oxime is theoretical (5.35 g.), with m.p. 143.5°. ²⁷

The Preparation of Nitrous Oxide

Nitrous oxide was prepared by the method of Victor Meyer ²⁸ as improved by Guye and Bogdan. ²⁹ The lower bulb of the generator had a capacity of 200 cc., and was charged with a solution of hydroxylamine sulphate (33 g. dissolved in 100 cc. distilled water, previously boiled and cooled); the upper bulb of the generator had a capacity of 100 cc. and was charged with a solution of sodium nitrite (30 g. in 40 cc. distilled water, previously boiled and cooled). The nitrous oxide produced in the reaction was passed through a purification train arranged as follows: first, a Milligan wash-bottle containing a solution of potassium hydroxide (150 g. reagent grade potassium hydroxide dissolved in 200 cc. distilled water, previously boiled and cooled); second, a Milligan wash-bottle containing a solution of α -naphthylamine and amino G-salt (150 cc. of a saturated aqueous solution of pure α -naphthylamine + 0.05 g. amino G-salt dissolved in 150 cc. water and 45 cc. pure acetic acid. The water used was previously boiled and cooled); third, two bubble-tubes in series, containing concentrated sulphuric acid; fourth, a phosphorus pentoxide drying tube. The whole apparatus was evacuated, then filled with nitrous oxide and evacuated again, this process being repeated six times to make sure of the purity of the nitrous oxide collected for use in the experimental work.

²⁷Lachman, op. cit.

²⁸Victor Meyer, Ann., 175, 141 (1875).

²⁹Guye and Bogdan, J. chim. phys., 3, 551 (1905).

The Preparation of Nitric Oxide

Nitric oxide was prepared by the method of Winkler,³⁰ using a generator similar to that employed in the preparation of nitrous oxide. The lower bulb was charged with a solution of potassium nitrite and potassium iodide (63 g. potassium nitrite in 50 cc. water + 26 g. potassium iodide in 25 cc. water); the upper bulb was charged with a solution of sulphuric acid (25.2 cc. concentrated acid in 25 cc. water). The gas generated was passed through a Milligan wash-bottle containing concentrated sulphuric acid. The whole apparatus was evacuated, then filled with nitric oxide and evacuated again, this process being repeated six times to make sure of the purity of the nitric oxide collected for use in the experimental work.

The Storage of Benzophenoneoxime

If benzophenoneoxime is kept for any length of time it generally decomposes. An oxime which is in the incipient stages of decomposition has a slightly lower melting point than the freshly-prepared oxime; furthermore, it gives a colour test with phenol and concentrated sulphuric acid. If a small particle of freshly-prepared benzophenoneoxime is placed in a test-tube, a small crystal of phenol added, and then 5 cc. concentrated sulphuric acid, no colour develops, even on long standing; but if this test is made on an oxime, the induction period of whose decomposition is coming to an end, a bright green colour develops, the intensity of the colour depending upon how far decomposition has progressed.

A sample of oxime, for which the decomposition has not proceeded to completion, may be recovered by recrystallization

³⁰Winkler, Ber., 34, 1408 (1901).

from dioxan and water. In a typical recrystallization of this kind, 5.4 g. oxime (m.p. 139-142°; positive colour test with phenol and sulphuric acid) was dissolved in 300 cc. dioxan; two litres of water were added, in small amounts over the space of an hour, to this solution, and, after standing for another hour, the precipitated oxime was collected on a sintered glass filter and washed well with cold water. The yield of oxime amounted to 4.82 g., with m.p. 143.5°.

A 1.5 g. sample of benzophenoneoxime was sealed in a tube in an atmosphere of carbon dioxide. After an interval of twelve months, the tube was opened. The oxime had melting point 141-143°, and gave a faintly positive colour with phenol and concentrated sulphuric acid.

A 1.3 g. sample of benzophenoneoxime was sealed in a tube in an atmosphere of air. After twelve months the tube was opened. The oxime had a brownish tinge, gave an intense green colour with phenol and concentrated sulphuric acid, and had the melting point 140-142°.

A 1.0 g. sample of benzophenoneoxime was sealed in a tube in an atmosphere of oxygen. After five months the tube was opened. The melting point of the oxime was 136-141°, and the green colour in the phenol-sulphuric acid test was very intense.

A 1.0 g. sample of benzophenoneoxime was sealed in a tube in an atmosphere of nitrous oxide. After five months the tube was opened. The melting point of the oxime was 141-143°, and the phenol-sulphuric acid test was negative.

A 1.0 g. sample of benzophenoneoxime was sealed in a tube in an atmosphere of nitric oxide. After five months the tube was opened. The melting point of the oxime was 141-143°, and the phenol-sulphuric acid test was positive.

In an atmosphere of the oxides of nitrogen, benzophenone-oxime decomposes rapidly, and gives a residue of brownish oil.

The Analysis of Hydroxylamine Hydrochloride

For the analysis of this substance by titration with potassium permanganate, the following solutions are required: 0.05 N potassium permanganate, 12 N sulphuric acid, ferric sulphate containing 57 g. anhydrous salt per litre.

The permanganate solution was prepared in the following way: Two litres of distilled water were heated to boiling and boiled for a few minutes to drive off dissolved gases; after cooling somewhat, 4 g. potassium permanganate was added; after standing for 24 hours, the solution was filtered through a sintered glass filter, and the filtrate standardized against sodium oxalate.³¹ The standardization was performed in the following way: Sodium oxalate, of tested purity (the sample used happened to be 99.76 % sodium oxalate) was dried at 140° for two hours; a 0.4 g. sample was accurately weighed out, dissolved in water, and the volume made up to the mark in a 50 ml. volumetric flask; 10 cc. samples of this solution were then pipetted into 200 cc. beakers, diluted to 100 cc., and heated to about 80°; to the hot solution, 20 cc. 2 N sulphuric acid was added, and the permanganate solution was then added from a burette, a similar beaker containing 150 cc. water being used as a standard of reference for the estimation of the end-point. A permanganate solution prepared in this way, and stored in an amber glass bottle, keeps fairly well; for example, one solution was standardized and found to be 0.05124 N; a month later, a restandardization gave the value 0.05114 N.

³¹Sørensen, *Zeit. anal. Chem.*, **42**, 352 and 512 (1903); *Ibid.*, **45**, 272 (1906).

The ferric sulphate solution was made up in the following way: Two litres of distilled water were heated to boiling, and then allowed to cool; when cool, 62 cc. concentrated sulphuric acid was added, and then 118 g. anhydrous ferric sulphate; this mixture was allowed to stand until dissolution was complete, and the liquid was then filtered through a sintered glass filter. The filtrate was stored in an amber glass bottle.

The analysis of the hydroxylamine hydrochloride was carried out in the following way: The dry salt (0.035 g.) was accurately weighed out, and dissolved in 50 cc. water in a 500 cc. lipped Erlenmeyer flask; 15 cc. 12 N sulphuric acid was added, and then 25 cc. ferric sulphate solution; the flask was closed with a funnel and the contents, after boiling for ten minutes and cooling in a stream of cold water, were diluted with 90 cc. water. The titration of the ferrous salt was then made, with the potassium permanganate solution, in the usual way; with a little practice, the end-point can be judged quite sharply. Blank analyses were made, the volumes of permanganate solution being measured with a micro-burette. The figures for a typical pair of analyses are given.

	(1)	(11)
Hydroxylamine hydrochloride:	0.034353 g.	0.033913 g.
0.05124 N permanganate:	19.13 cc.	18.91 cc.
Blank analysis:	0.06 cc.	0.06 cc.
Percent hydroxylamine hydrochloride:	99.19	99.33

For the analysis of hydroxylamine hydrochloride by titration with potassium hydroxide, 1 N potassium hydroxide is required. This was standardized against a standard sulphuric acid, whose normality had been determined with sodium carbonate. For

the analysis, 1 g. hydroxylamine hydrochloride is weighed out accurately, dissolved in 100 cc. water, and a drop of phenolphthalein added; the potassium hydroxide is then run in from a burette. The figures for a typical pair of analyses are shown.

	(i)	(ii)
Hydroxylamine hydrochloride:	0.9991 g.	0.9996 g.
0.8670 N potassium hydroxide:	16.45 cc.	16.46 cc.
Percent hydroxylamine hydrochloride:	99.19	99.19

Determination of Hydroxylamine Hydrochloride in the Presence of Acetic Acid

These analyses were performed in a similar manner to those described in the preceding section, except that 25 cc. acetic acid was also present in the solution. A 0.03 g. sample of hydroxylamine hydrochloride was accurately weighed out and dissolved in 25 cc. water in a 500 cc. wide-mouthed, lipped Erlenmeyer flask; to this solution, 25 cc. of the acetic acid under examination was added from a pipette, 15 cc. 12 N sulphuric acid, and 25 cc. ferric sulphate solution; the contents of the flask were then boiled for 10 minutes. This liquid possesses the property of "bumping" in a most unpleasant degree, and the presence of boiling beads does not altogether overcome it. A very convenient and efficient method of eliminating this trouble was found by using a filter funnel of the right diameter to close the mouth of the flask, the stem being of such a length that the tip of the funnel barely touches the bottom of the flask as the funnel hangs suspended in the flask's mouth; the stem of the funnel is closed completely, by heating in a small flame until the walls fall together, at a point some 2 1/2 cm. from the tip. This provides a constant stream of vapour bubbles through the

liquid, and the boiling proceeds with perfect smoothness. When the boiling was completed, the flask and contents were cooled by standing in a stream of cold water, and the funnel was rinsed off, the few drops of liquid enclosed in the funnel's tip being readily removed by the use of a wash-bottle with a turned-up nozzle. The contents of the flask were then diluted with 95 cc. distilled water, and the ferrous salt was titrated with 0.05 N potassium permanganate. Blank analyses were made using a micro-burette. The figures for some of the analyses are given.

- (a) In the presence of General Chemical Company's acetic acid, labelled "U. S. P."

	(i)	(ii)
Hydroxylamine hydrochloride:	0.034435 g.	0.034257 g.
Potassium Permanganate (0.05124 N):	19.75 cc.	19.66 cc.
Blank analysis:	0.15 cc.	0.15 cc.
Percent hydroxylamine hydrochloride:	101.4	101.4

- (b) In the presence of Merck's acetic acid, labelled "Reagent Grade"

	(i)	(ii)
Hydroxylamine hydrochloride:	0.034219 g.	0.035312 g.
Potassium permanganate (0.05124 N):	19.87 cc.	20.61 cc.
Blank analysis:	0.16 cc.	0.16 cc.
Percent hydroxylamine hydrochloride:	102.6	103.1

	(iii)	(iv)
Hydroxylamine hydrochloride:	0.011922 g.	0.075125 g.
Potassium permanganate (0.05124 N):	7.18 cc.	43.14 cc.
Blank analysis:	0.16 cc.	0.16 cc.
Percent hydroxylamine hydrochloride:	104.9	101.9

- (o) In the presence of Mallinckrodt's acetic acid, labelled "C. P."

	(i)	(ii)
Hydroxylamine hydrochloride:	0.034381 g.	0.034577 g.
Potassium permanganate (0.05124 N):	19.77 cc.	19.80 cc.
Blank analysis:	0.27 cc.	0.27 cc.
Percent hydroxylamine hydrochloride:	100.8	100.6

- (d) In the presence of Kahlbaum's 100 % acetic acid, labelled "zur Analyse".

	(i)	(ii)
Hydroxylamine hydrochloride:	0.034795 g.	0.035100 g.
Potassium permanganate (0.05124 N):	19.56 cc.	19.68 cc.
Blank analysis:	0.16 cc.	0.16 cc.
Percent hydroxylamine hydrochloride:	99.28	99.04

- (e) In the presence of the Niacet Chemicals Corporation's synthetic acetic acid, labelled "U. S. F. Reagent".

	(i)	(ii)
Hydroxylamine hydrochloride:	0.033882 g.	0.034049 g.
Potassium permanganate (0.06086 N):	16.02 cc.	16.09 cc.
Blank analysis:	0.11 cc.	0.11 cc.
Percent hydroxylamine hydrochloride:	99.33	99.26

	(iii)	(iv)
Hydroxylamine hydrochloride:	0.073799 g.	0.011932 g.
Potassium permanganate (0.06086 N):	34.77 cc.	5.71 cc.
Blank analysis:	0.11 cc.	0.11 cc.
Percent hydroxylamine hydrochloride:	99.33	99.28

The Fractional Distillation of Acetic Acid

The fractional distillation of the acetic acid was carried out using a Snyder³² column fitted with a suitable

³²Hill and Ferris, op. cit.

dephlegmator. The effective length of the column was 700 mm., and it was surrounded by a vacuum jacket of 36 mm. diameter carrying a vacuum of about 10^{-3} mm. The column had a diameter of 20 mm., and was equipped with twelve balls placed at intervals of 50 mm. The balls were all of the same weight, and were made so that they would just float in water and just sink in toluene. The diameter of each ball was 13 mm., and the length of the tail 20 mm. A stream of warm water was run very slowly through the outer jacket of the dephlegmator, and, by a suitable regulation of the rate of flow, it was possible to adjust the reflux ratio to any desired value.

Since the anhydrous acid is extremely hygroscopic, it is necessary, during the course of a distillation, to protect the vent of the distillation apparatus from atmospheric moisture: a combination of calcium chloride and phosphorus pentoxide drying tubes works very well.

The freezing point of the anhydrous acid was found to be 16.70° . This freezing point was measured without transferring the acid from the receiver into which it had been distilled: almost two litres of the anhydrous acid was cooled to a temperature of 10° , and crystallization started on touching the side of the flask with the thermometer. The temperature rose quickly and after a short time had reached the value 16.70° , at which it remained stationary for over three-quarters of an hour. The temperature was read on a vacuum-jacketed thermometer, which was graduated to tenths of a degree and had been checked against a Bureau of Standards thermometer.

The boiling point, at 760 mm. pressure, of the 100.00 % acid was found to be 118.3° .

The density, measured with a pycnometer, and calculated

from the formula

$$d_{4^{\circ}}^{25^{\circ}} = \frac{\text{weight of acid at } 25^{\circ} \times 0.9971}{\text{weight of water at } 25^{\circ}}$$

was found to be 1.044. This agrees with the value calculated from the following equation, given in International Critical Tables;³³

$$d_t = d_s + 10^{-3}\alpha(t - t_s) + 10^{-6}\beta(t - t_s)^2 + 10^{-9}\gamma(t - t_s)^3$$

The Absorption Spectrum of Acetic Acid

The determination of the percentage of light transmitted in the ultra-violet region by three of the acetic acids studied, as compared with that transmitted by water, was measured with a photo-electric spectrophotometer.³⁴ The figures obtained are recorded in the following table.

Wave Length (Å)	Percentage of Light Transmitted		
	100.00 % Niacet Acid	Kahlbaum's 100 % Acid	Merck's Reagent Grade Acid
2200	5.4	3.6	4.4
2300	3.1	2.3	2.5
2400	2.5	1.8	2.0
2500	2.6	2.3	2.5
2525	8.9	7.3	6.6
2550	28.0	23.7	22.4
2575	53.8	45.5	44.0
2600	70.3	59.5	58.1
2700	89.5	77.7	76.0
2800	91.0	80.0	82.5
2900	92.5	82.1	87.0
3000	94.0	85.0	90.5
3100	96.0		
3200	96.0		

³³International Critical Tables, 3, p. 28.

³⁴Hogness, Zscheile, and Sidwell, op. cit.

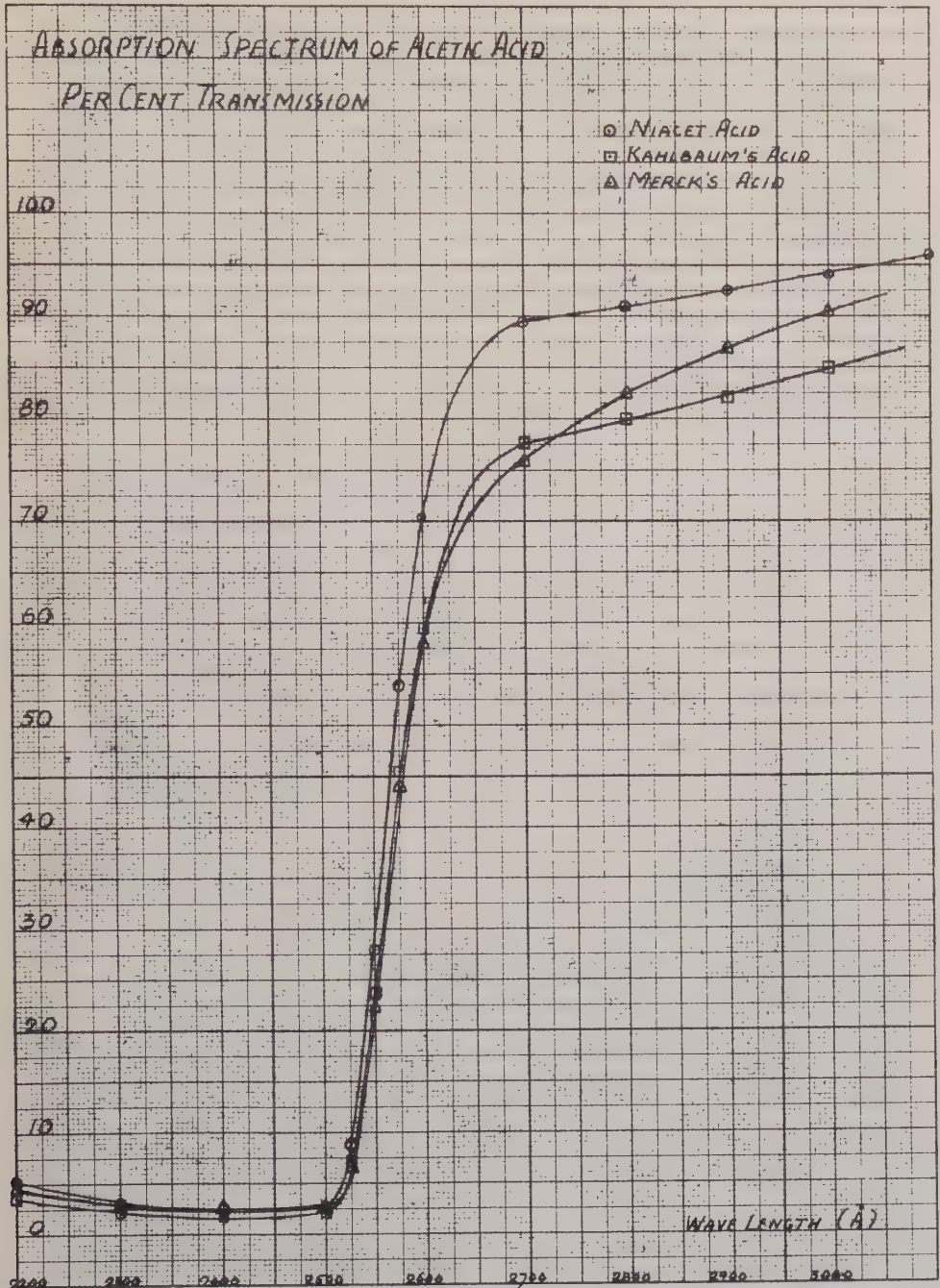


Fig. 2

The Analysis of Benzophenoneoxime

The method of performing this analysis was as follows: Benzophenoneoxime (0.023 g.) was accurately weighed out and dissolved in 10 cc. 100.00 % acetic acid in a 500 cc. wide-mouthed lipped Erlenmeyer flask; immediately on dissolution, 50 cc. distilled water was added, then 15 cc. 12 N sulphuric acid and 25 cc. ferric sulphate solution. From this point, the procedure was exactly the same as that described in the section "The Analysis of Hydroxylamine Hydrochloride", except that the ferrous sulphate was determined by titration with 0.01 N potassium permanganate solution.

This permanganate solution was made by diluting 405 cc. of the 0.05 N potassium permanganate to a volume of two litres with distilled water, which previously had been boiled and allowed to cool. After standing for twenty-four hours, this solution was filtered through a sintered glass filter and the filtrate standardized against sodium oxalate as described in the standardization of 0.05 N potassium permanganate, except that the sodium oxalate solution is prepared by weighing out accurately a 0.4 g. sample of sodium oxalate, dissolving it in water, and making up the volume to the mark in a 250 ml. volumetric flask. A permanganate solution prepared in this way, and stored in an amber glass bottle, keeps very well; for example, a solution was standardized and its composition determined as 0.01012 N; two weeks later a standardization gave the value 0.01009 N.

The figures for two typical pairs of analyses on different preparations of benzophenoneoxime are given.

(a)	(i)	(ii)
Benzophenoneoxime:	0.021963 g.	0.023774 g.
Potassium permanganate (0.01016 N):	22.24 cc.	24.03 cc.
Blank analysis:	0.27 cc.	0.27 cc.
Percent nitrogen:	7.115	7.111

(b)	(i)	(ii)
Benzophenoneoxime:	0.02302 g.	0.02302 g.
Potassium permanganate (0.01051 N):	22.13 cc.	22.11 cc.
Blank analysis:	0.43 cc.	0.46 cc.
Percent nitrogen:	7.076	7.069

Calculated percentage nitrogen: 7.108

The Analysis of p,p'-dimethoxybenzophenoneoxime

This analysis is performed in a similar way to that of benzophenoneoxime. The figures for pairs of analyses on two different preparations of this oxime are given.

(a)	(i)	(ii)
p,p'-dimethoxybenzophenoneoxime:	0.030526 g.	0.031135 g.
Potassium permanganate (0.009847 N):	24.87 cc.	25.27 cc.
Blank analysis:	0.52 cc.	0.52 cc.
Percent nitrogen:	5.504	5.484

(b)	(i)	(ii)
p,p'-dimethoxybenzophenoneoxime:	0.030509 g.	0.031113 g.
Potassium permanganate (0.00984 N):	24.46 cc.	24.52 cc.
Blank analysis:	0.39 cc.	0.39 cc.
Percent nitrogen:	5.508	5.505

Calculated percentage of nitrogen: 5.449

The Rate of Change of the Concentration of Benzophenoneoxime in Acetic Acid Solution

A 0.25 g. sample of dry and freshly-prepared benzophenoneoxime was weighed out in a 25 cc. beaker. It was dissolved in 99.90 % acetic acid at 25.00°, the time at the instant of dissolution being noted as the initial time of the reaction. The acetic acid solution was quickly added to more of the same acetic acid, also at 25.00°, in a 200 ml. volumetric flask, the beaker being rinsed out thoroughly with more of the same acetic acid from a small wash-bottle. The solution in the volumetric flask was diluted to the mark with more of the same acetic acid, and, after thorough mixing, was transferred to a glass-stoppered, 250 cc. Erlenmeyer flask, which was placed in a thermostat at 25.00°. This entire operation was done as rapidly as possible, and did not take more than five minutes.

In order to determine the concentration of benzophenoneoxime in the solution at any particular moment, a sample was withdrawn from time to time, with a 10 cc. pipette, and placed in a wide-mouthed, lipped, 500 cc. Erlenmeyer flask, and 50 cc. water was added. The time was noted at the moment of adding the water, for that stops any further transformation of the oxime. Then, to the contents of the Erlenmeyer flask, 15 cc. 12 N sulphuric acid and 25 cc. ferric sulphate solution were added, and the subsequent procedure was exactly similar to that described in the section on the analysis of benzophenoneoxime.

From time to time, a 1 cc. sample was withdrawn by means of a pipette from the liquid in the reaction flask, placed in a test-tube, and 3 cc. water added, the time being noted at the moment of adding the water. To the contents of the test-tube, 4 cc. α -naphthylamine solution and 4 cc. amino G-salt solution were

then added. The contents of the tube were then heated to boiling and allowed to cool. The appearance of a pale pink colour signifies the approach of the end of the induction period; and since at this time the samples for quantitative analysis should be withdrawn every few minutes, it is very helpful to have that information. The absence of any colour in the test shows that the induction period is not over, and the development of an intense purple-red colour shows that the reaction is well on its way. It is better to use conductivity water in making all these tests for the presence of nitrite ion, for distilled water generally contains enough nitrite ion to give a pale pink colour.

The α -naphthylamine solution was prepared in the following way: Commercial α -naphthylamine was recrystallized several times by allowing a hot ligroin (b.p. 36°) solution to cool; 10 g. α -naphthylamine in 350 cc. ligroin is a convenient solution to start with. In an Erlenmeyer flask, with a loosely-fitting glass stopper, 150 cc. conductivity water was heated to boiling, boiled a few minutes, and then allowed to cool somewhat. To the hot water, 0.15 g. of the recrystallized α -naphthylamine was added, the contents of the flask again heated to boiling, and after the boiling had been continued for a few minutes, the flask was stoppered and set aside to cool.

The amino G-salt solution was prepared by adding 0.05 g. amino G-salt (Eastman) to 150 cc. conductivity water, previously boiled and cooled. After the dissolution of the salt, 45 cc. pure acetic acid was added.

It is important to protect both these solutions from the atmosphere of a chemical laboratory, especially from the oxides of nitrogen.

The figures obtained in two typical sets of rate measure-

ments made in this way are recorded in the following tables, and graphs of the results are given (Figs. 3 and 4).

(a) Benzophenoneoxime: 0.2507 g. per 200.00 cc.

Volume of samples: 9.93 cc.

Concentration of permanganate: 0.01016 N.

Blank analysis: 0.22 cc.

Time (minutes)	Titration (cc.)
0	.12.50*
10	.12.80
131	.12.78
170	.12.81
198	.12.76
210	.12.15
219	.10.71
231	5.32
235	4.50
240	2.83
246	2.62
251	1.24
256	1.05
266	1.00
278	0.78
290	0.78
1269	0.20

(b) Benzophenoneoxime: 0.2493 g. per 200.0 cc.

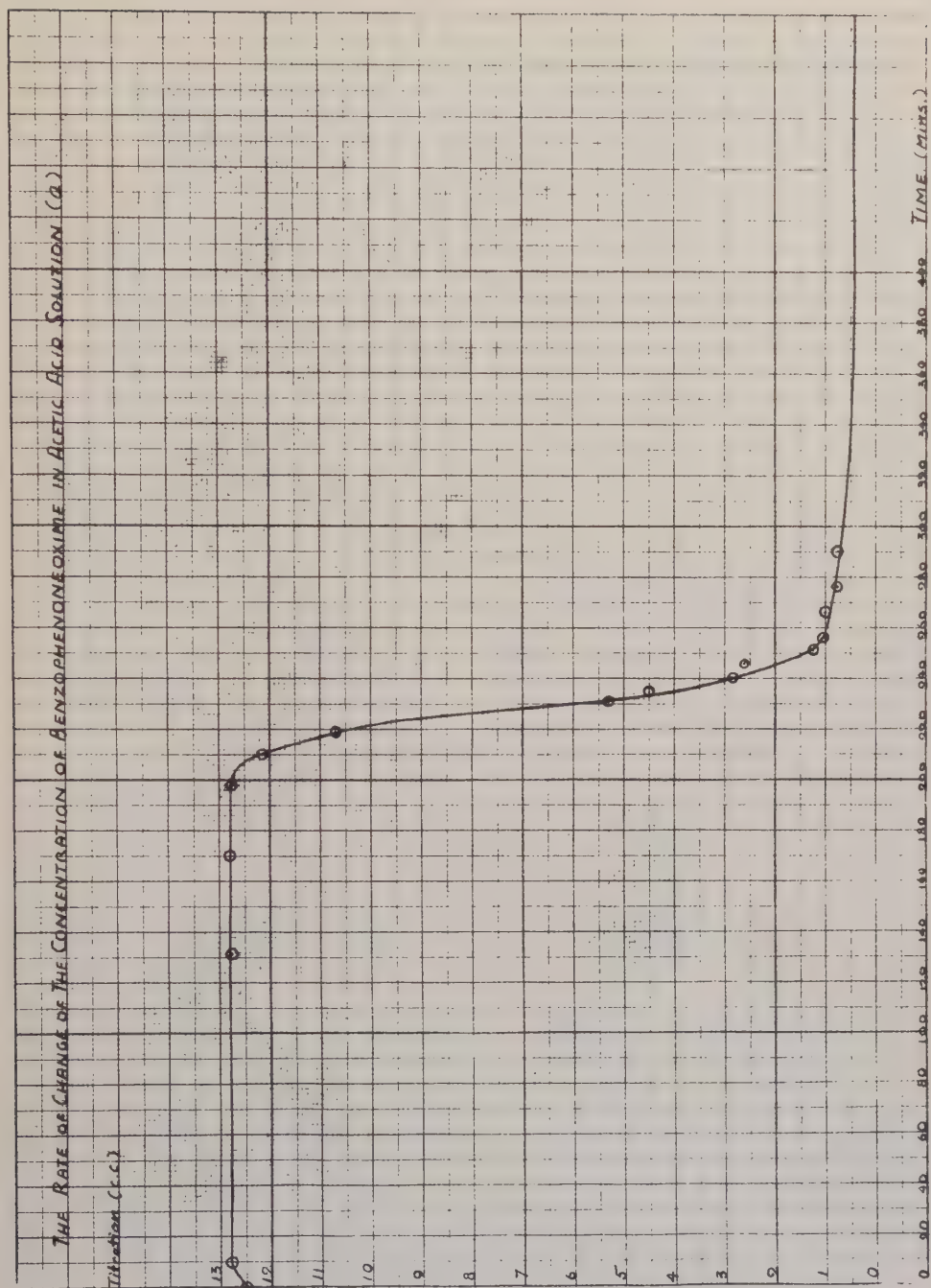
Volume of samples: 10.00 cc.

Concentration of permanganate: 0.009966 N.

Blank analysis: 0.31 cc.

Time (minutes)	Titration (cc.)
0	.12.70*
77	.13.05
186	.13.39
271	.13.04
399	.13.14
568	.12.27
578	.11.26
584	.10.23
589	8.94
594	7.63
601	6.01
610	6.04
628	2.61
675	0.58
704	0.33
776	0.21

*Calculated



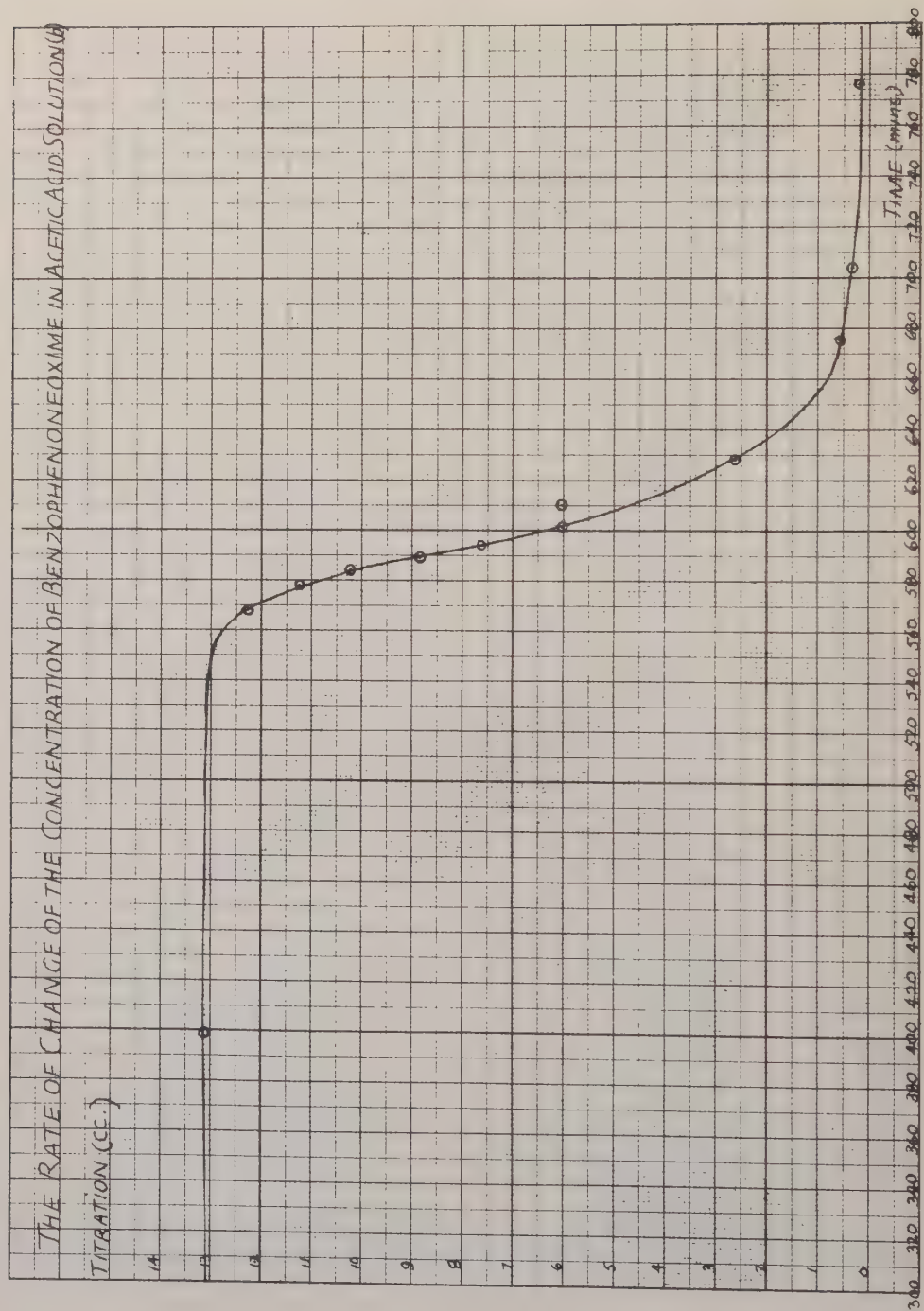


Fig. 4

The Constancy of the Induction Period

Two similar rate runs were made on the same oxime, using the same acetic acid as a solvent, the conditions, so far as is known, being similar for each. The measurements show that the induction period is practically constant (Fig. 5).

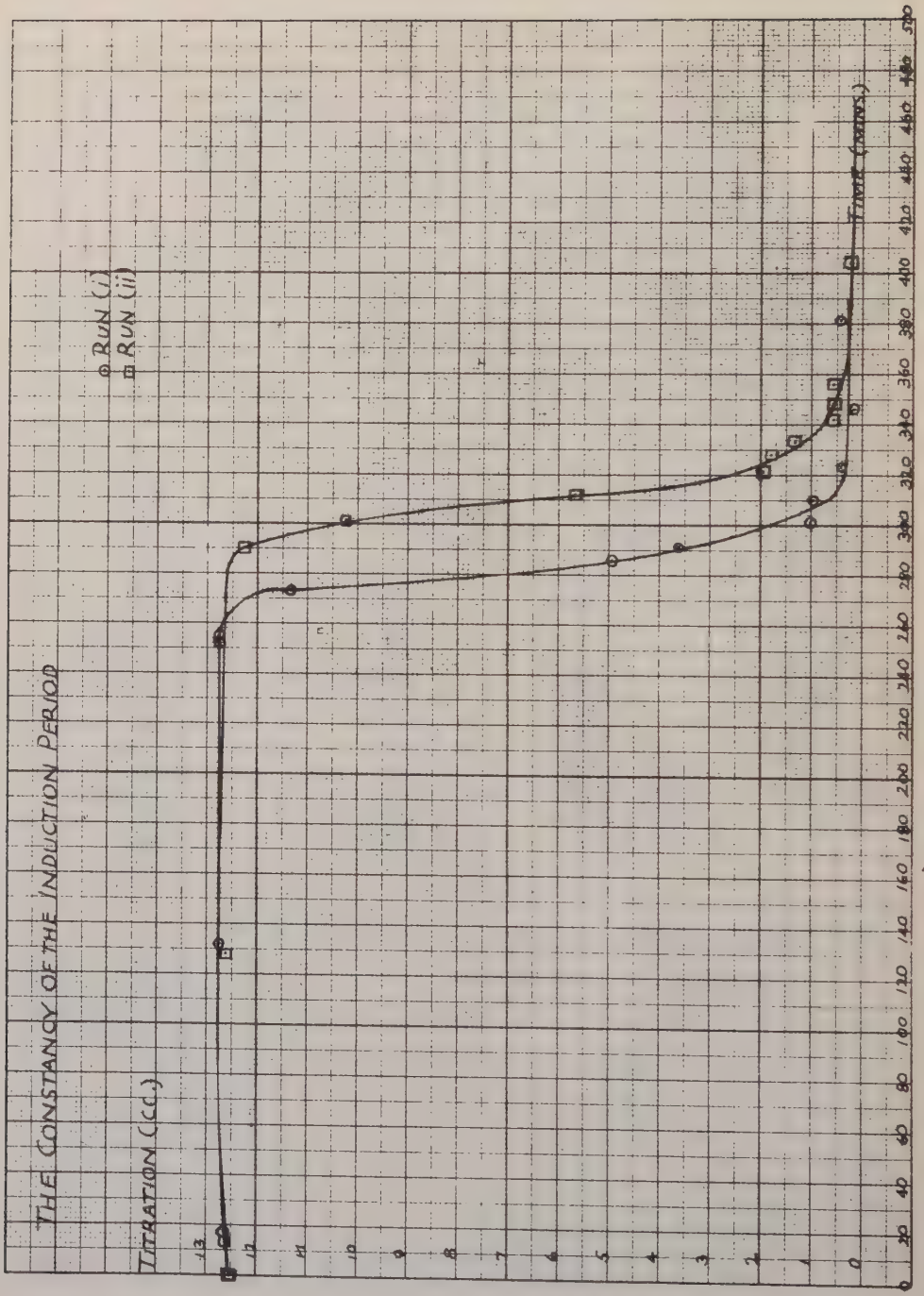
	(i)	(ii)
Benzophenoneoxime:	0.2494 g. per 200.00 cc.	0.2492 g. per 200.00 cc.
Volume of samples:	10.00 cc.	9.99 cc.
Concentration of permanganate:	0.01010 N	0.01010 N
Blank analysis:	0.35 cc.	0.35 cc.

(1)		(11)	
Time (minutes)	Titration (cc.)	Time (minutes)	Titration (cc.)
0	12.53*	0	12.52*
17	12.65	13	12.63
132	12.73	128	12.62
255	12.78	252	12.76
273	11.32	290	12.28
286	4.46	301	10.24
291	3.62	312	5.68
301	1.02	321	1.95
310	0.98	328	1.80
323	0.42	333	1.33
346	0.69	342	0.58
381	0.42	348	0.58
		356	0.58
		404	0.23

The Effect of Sodium Nitrite on the Induction Period

Two similar runs were made, as in the work recorded in the previous section, but to run (ii) 0.000090 g. sodium nitrite was added 32 minutes after zero time (Fig. 6).

*Calculated



	(i)	(ii)
Benzophenoneoxime:	0.2497 g. per 200.00 cc.	0.2493 g. per 200.00 cc.
Volume of samples:	10.01 cc.	9.93 cc.
Concentration of permanganate:	0.01016 N	0.01016 N
Blank analysis:	0.22 cc.	0.22 cc.

(i)		(ii)	
Time (minutes)	Titration (cc.)	Time (minutes)	Titration (cc.)
0	12.43*	0	12.40*
7	12.50	8	12.71
16	12.81	16	12.93
24	12.67	79	12.86
81	12.70	86	12.74
189	12.79	96	12.75
211	12.69	106	12.43
220	12.55	120	10.74
229	12.30	127	6.91
238	11.29	133	4.21
245	7.65	137	2.99
251	5.17	140	2.30
255	3.57	145	0.43
258	3.05	158	0.14
263	1.77	328	0.12
268	1.09	1244	0.13
279	0.19		
372	0.59		
1255	0.33		

The Effect of Nitrous Oxide on the Induction Period

The nitrous oxide was prepared as described, and a quantity collected in a thin-walled bulb of measured capacity. At a suitable moment, a bulb was broken beneath the reaction liquid in one of a pair of runs, and by subsequent analyses the effect of the gas on the induction period determined. In run (ii) of pair A (Fig. 7) 0.000176 g. nitrous oxide was added 73 minutes after zero time: in run (ii) of pair B (Fig. 8) 0.000123 g. nitrous oxide was added 39 minutes after zero time.

*Calculated

	(i)	(ii)
Benzophenoneoxime:	0.2498 g. per 200.0 cc.	0.2514 g. per 200.0 cc.
Volume of samples:	10.00 cc.	9.99 cc.
Concentration of permanganate:	0.01010 N	0.01010 N
Blank analysis:	0.35 cc.	0.35 cc.

(i)		(ii)	
Time (minutes)	Titration (cc.)	Time (minutes)	Titration (cc.)
0	12.54*	0	12.63*
15	13.15	13	13.13
50	12.74	46	12.74
125	13.06	71	12.96
238	12.74	89	12.96
312	12.30	160	12.84
316	11.94	202	10.96
320	11.52	207	9.47
325	9.89	212	6.62
330	6.88	215	5.46
334	5.13	219	4.01
338	3.43	222	2.66
343	1.57	235	1.31
348	1.03	249	0.63
354	0.70	277	0.43
362	0.74	399	0.32
374	0.60		

	(i)	(ii)
Benzophenoneoxime:	0.2490 g. per 200.0 cc.	0.2503 g. per 200.0 cc.
Volume of Samples:	10.00 cc.	9.99 cc.
Concentration of permanganate:	0.01010 N	0.01010 N
Blank analysis:	0.35 cc.	0.35 cc.

(i)		(ii)	
Time (minutes)	Titration (cc.)	Time (minutes)	Titration (cc.)
0	12.51*	0	12.56*
14	12.60	11	12.81
101	12.96	33	12.76
201	12.76	45	12.83
308	12.61	91	12.78
317	12.07	191	12.80
324	11.33	254	12.57
329	9.75	260	12.37
334	7.11	266	11.92
342	3.19	272	10.73
345	2.15	277	7.13
351	1.20	282	4.67
356	0.59	287	2.68
361	0.59	292	0.95
372	0.65	297	0.61
438	-0.10	304	0.67
		314	0.22
		342	0.39

*Calculated

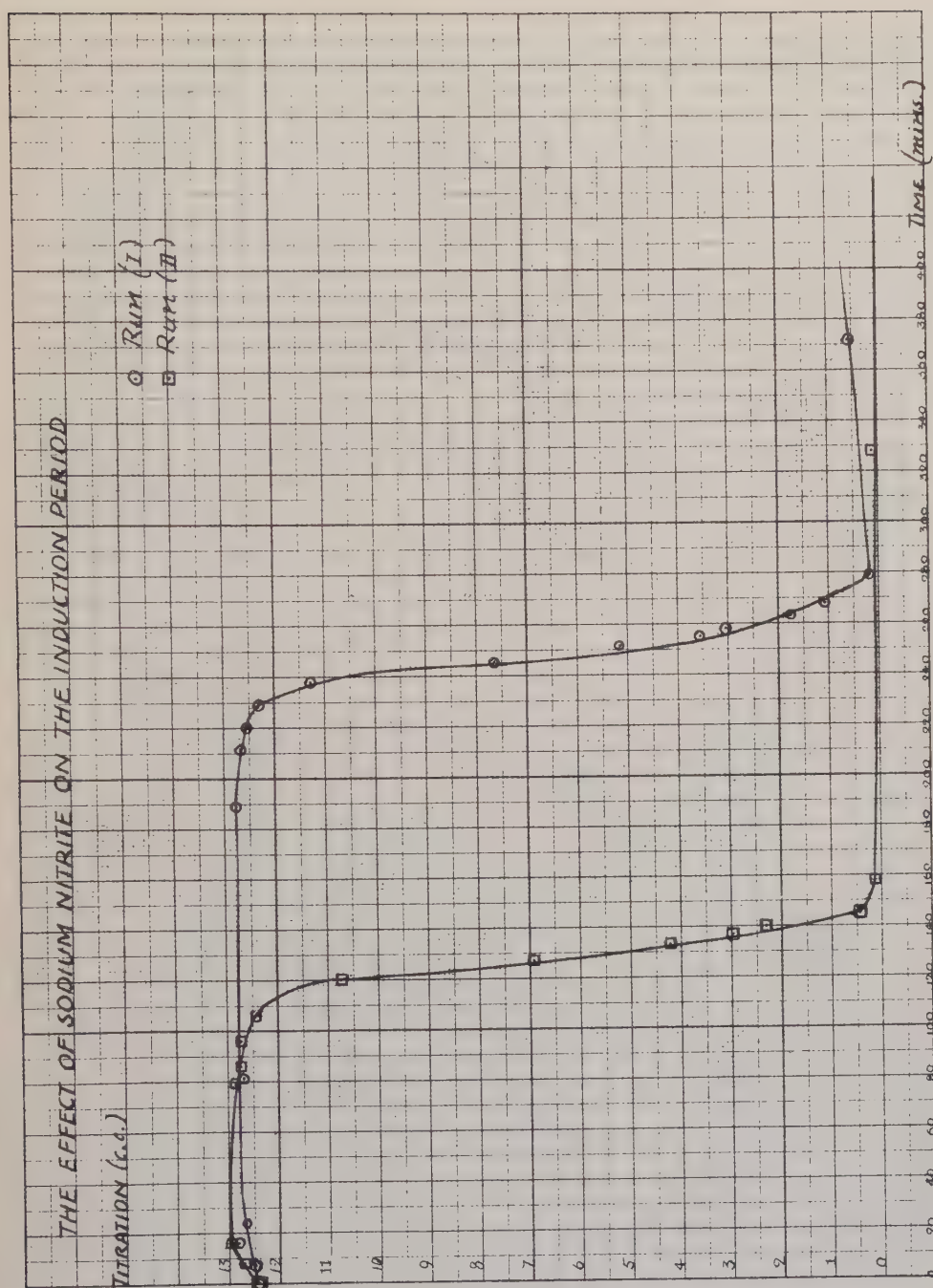
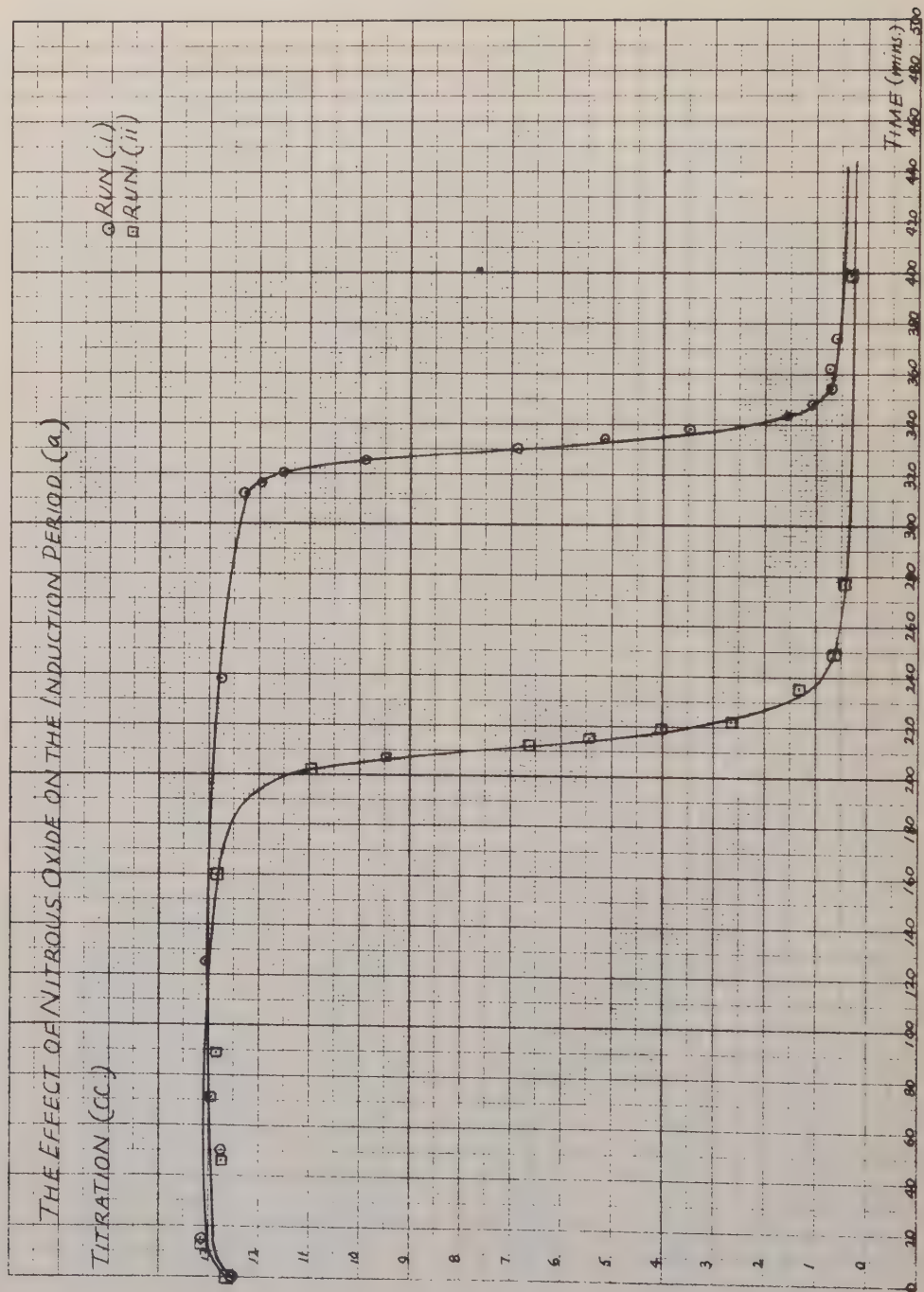
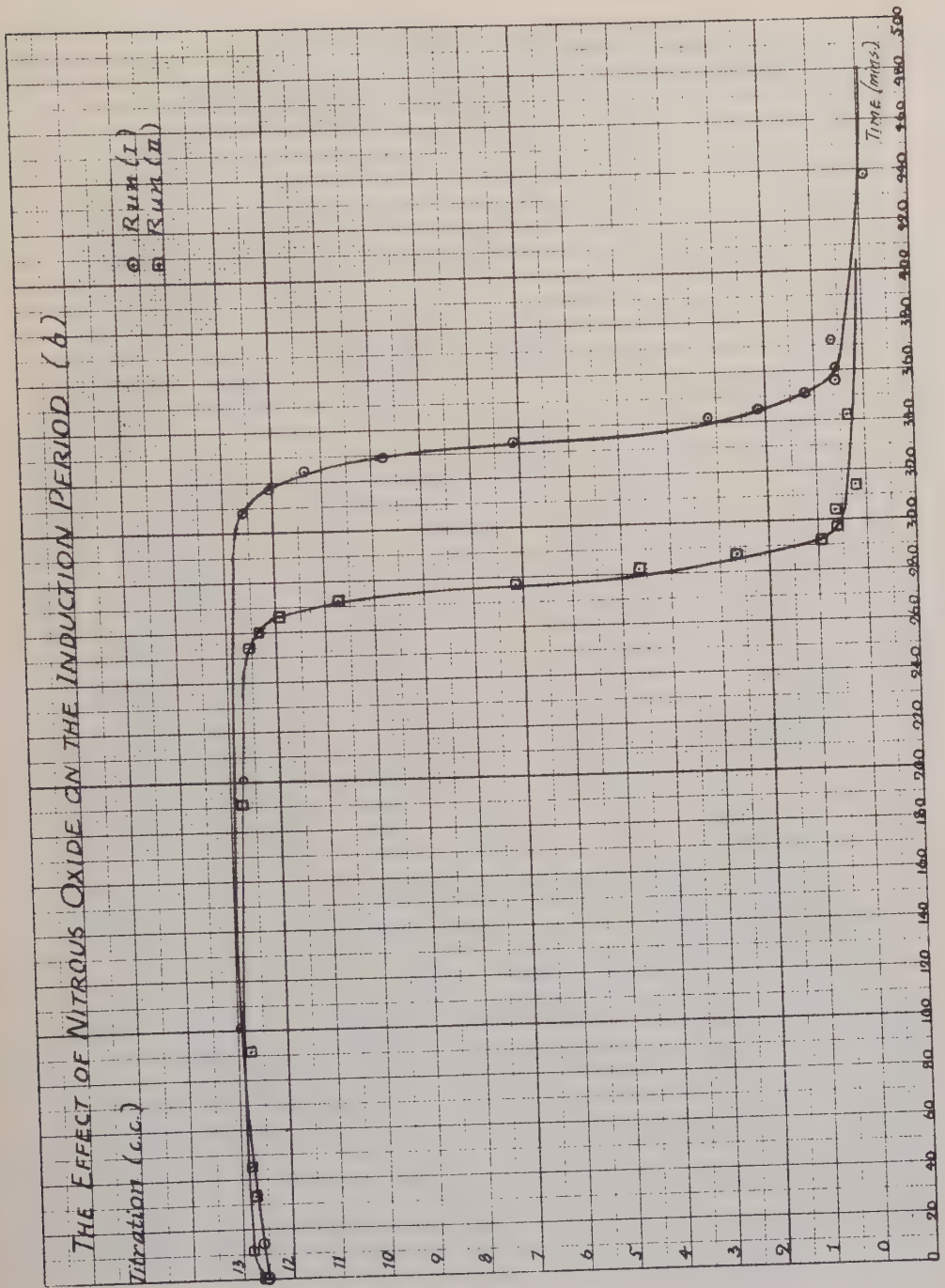


Fig. 6





The Effect of Acetanilide on the Induction Period

A similar pair of runs were made, and in run (ii) of the pair, 0.000629 g. acetanilide was added 75 minutes after zero time. No effect on the induction period was observed (Fig. 9).

	(i)	(ii)
Benzophenoneoxime:	0.2490 g. per 200.0 cc.	0.2503 g. per 200.0 cc.
Volume of samples:	10.00 cc.	10.01 cc.
Concentration of permanganate:	0.01007 N	0.01007 N
Blank analysis:	0.22 cc.	0.22 cc.

(i)		(ii)	
Time (minutes)	Titration (cc.)	Time (minutes)	Titration (cc.)
0	12.54*	0	12.61*
65	12.77	57	13.07
136	12.92	112	12.85
247	12.77	246	12.80
254	12.58	256	12.45
264	12.01	267	10.94
274	8.40	277	6.16
285	4.25	285	3.84
295	1.67	293	2.72
303	0.85	301	1.08
313	0.68	312	0.85
367	0.49	357	0.60

The Effect of Water on the Induction Period

The most important single factor governing the decomposition of benzophenoneoxime in acetic acid solution appears to be the water content of the solvent acid. The nitrite ion test, which has been used as a qualitative indication of the end of the induction period in the reaction-rate measurements recorded in this paper, yields additional information in a qualitative sort of way. For instance, when a 1 cc. sample of reaction liquid of the concentration used in this study is placed in a test-tube and diluted with 3 cc. water, if a cloudiness appears, the transfor-

* Calculated

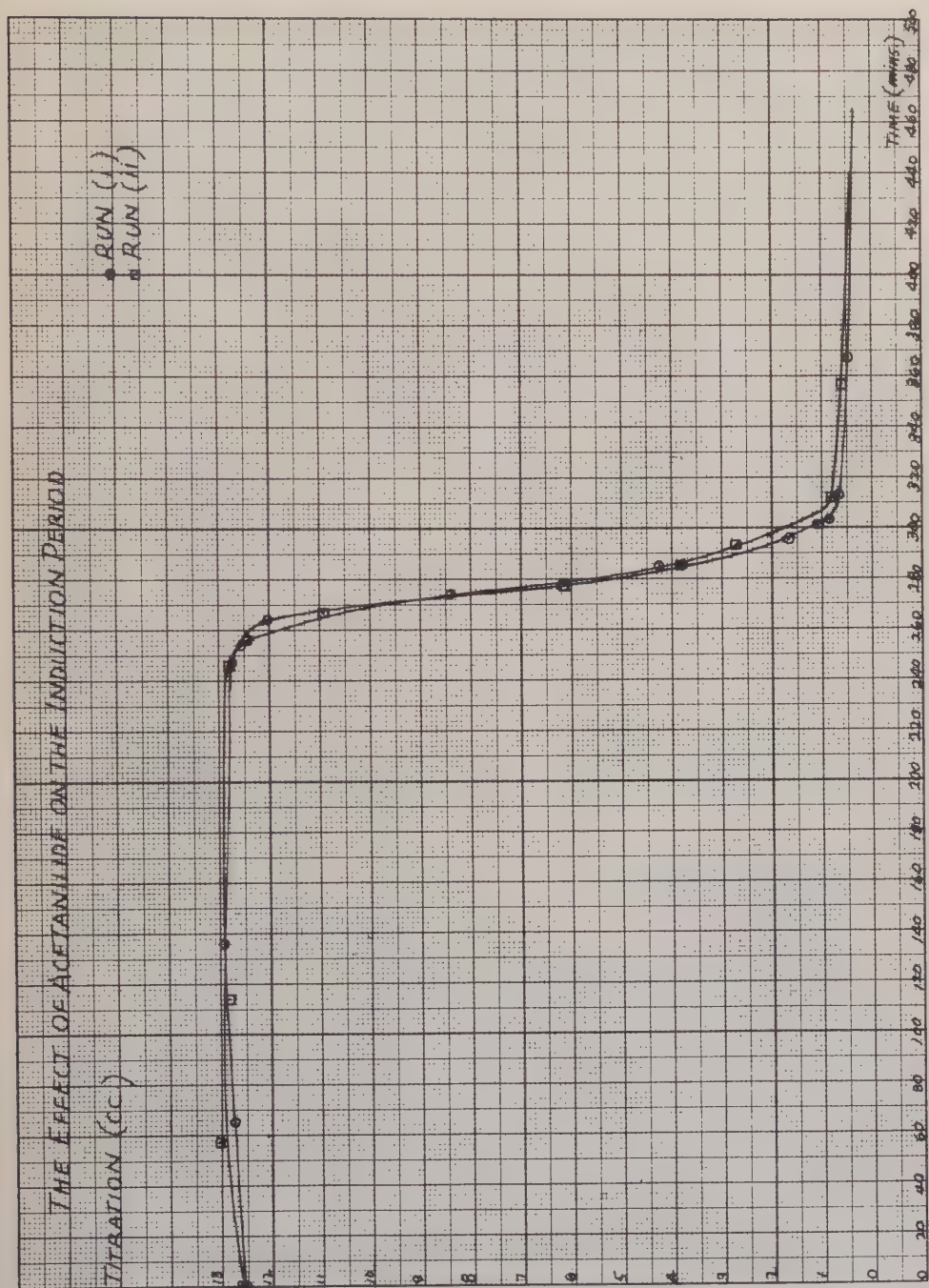


Fig. 9

mation of the oxime is complete. If, however, the cloudiness does not appear until the addition of the 4 cc. α -naphthylamine solution, the transformation is not complete but is well on its way (perhaps two-thirds complete). If no cloudiness appears on the addition of the α -naphthylamine solution, but a positive colour is obtained when the nitrite ion test is made, the induction period is over, but the transformation is less than two-thirds complete.

This provided a rapid and easy method of gaining qualitative information concerning the behaviour of any particular oxime in any particular acid. A suitable amount of the particular benzophenoneoxime (0.0125 g.) was placed in a glass-stoppered test-tube, and 10 cc. of the particular acetic acid was added from a pipette. As before, the time of dissolution was noted as zero time, the stoppered test-tube was placed in a thermostat at 25.00° and, at intervals, 1 cc. samples were withdrawn and the nitrite ion test performed.

Tests made in this way, upon acids of differing water content, gave the following qualitative results:

	(i)	(ii)
Benzophenoneoxime:	0.0131 g.	0.0135 g.
Solvent:	100.00 % acid	99.90 % acid
Induction period:	> 18 hours	< 4 hours
Completeness of reaction:	Test negative	Complete in 6 hours
	(iii)	(iv)
Benzophenoneoxime:	0.0124 g.	0.0120 g.
Solvent:	99.50 %	99.84 % acid
Induction period:	> 26 hours	2 1/2 hours
Completeness of reaction:	Test negative	Complete in 5 hours

The Rate of Change of the Concentration of Nitrite Ion in an Acetic Acid Solution of Benzophenoneoxime

The Stieglitz-Palmer³⁵ modification of the Ilosvay³⁶ test may be used to measure quantitatively the concentration of nitrite ion in a solution with the aid of a colorimeter. This was done in one experiment and the results are recorded in the following table, of which a graph has been plotted (Fig. 10). No attempt was made to measure the actual concentration of nitrite ion, but simply to determine its rate of change, which is inversely proportional to the rate of change of the colorimeter readings. A 1 cc. sample of the reaction liquid was transferred to a test-tube with a pipette, and 3 cc. conductivity water added from a pipette, the time being noted at the moment of dilution; then 4 cc. α -naphthylamine solution was added from a pipette, followed by 4 cc. amino G-salt solution from a pipette. The test-tube and its contents were placed in a water bath at 100° for five minutes, then cooled at 0° for five minutes, and the colorimetric measurement made at once. The standard of comparison was made up by dissolving 0.0102 g. sodium nitrite in conductivity water, and diluting in a volumetric flask to a volume of 100.0 cc.; a 0.500 cc. sample of this solution was then taken and diluted with 3.50 cc. conductivity water: the addition of 4 cc. α -naphthylamine solution and then of 4 cc. amino G-salt solution, and the subsequent development of the colour, were done in the way described for the tests on the reaction liquid.

³⁵Stieglitz and Palmer, op. cit.

³⁶Ilosvay, op. cit.

Benzophenoneoxime: 0.2499 g. per 200.0 cc.

Time (minutes)	R Dial Reading on Colorimeter. (mm.)	$\frac{1}{R} \times 2^*$
0	∞	0
17	∞	0
88	∞	0
134	∞	0
145	85.25	0.2346
154	20.62	0.9700
164	11.79	1.6960
175	15.27	1.3096
184	20.24	0.9882
194	25.50	0.7844
205	35.48	0.5636
220	38.68	0.5170
241	39.64	0.5046
276	50.14	0.3990
329	55.58	0.3598
387	57.72	0.3464
516	69.14	0.2892

The Relationship between the Changes in Concentration of Nitrite Ion and of Benzophenoneoxime

Two experiments were performed in which the rates of change in concentration of both nitrite ion and oxime were measured. The measurements were made by the methods already described, and the results are given in the two following tables. Graphs are given for these figures, the two curves for each experiment being on one graph (Figs. 11 and 12).

*The factor 2 is for convenience in plotting.

(1)

Benzophenoneoxime: 0.3126 g. per 250.0 cc.
 Volume of samples: 9.99 cc. for oxime; 1 cc.
 for nitrite ion
 Concentration of permanganate: 0.01080 N
 Blank analysis: 0.38 cc.

Time (minutes)	Titration (cc.)	R Dial Reading on Color- imeter (mm.)	$2 \times \frac{1}{R} \times 10^2^*$
0	11.73**	∞	0
7		∞	0
13	12.20		
29	12.25		
33		∞	0
60	12.29		
63		∞	0
121	12.06		
124		1075	0.186
145	11.76		
148		131.0	1.42
158		35.0	5.8
163		12.7	15.8
168		13.8	14.6
173	5.72		
176		11.4	17.6
181		11.1	18.0
186	3.94		
189		11.6	17.2
194		11.0	18.2
199	2.94		
203	2.57		
207	1.92		
210		11.8	17.0
217	1.24		
226		11.6	17.2
234	0.55		
251	0.37		
255		11.3	17.8
283	0.33		
287		14.9	13.4
334	0.30		
337		18.7	10.6
506	0.14		
510		27.0	7.4
1612	0.23		
1615		34.0	5.8

* The factor 2×10^2 is for convenience in plotting.

**Calculated

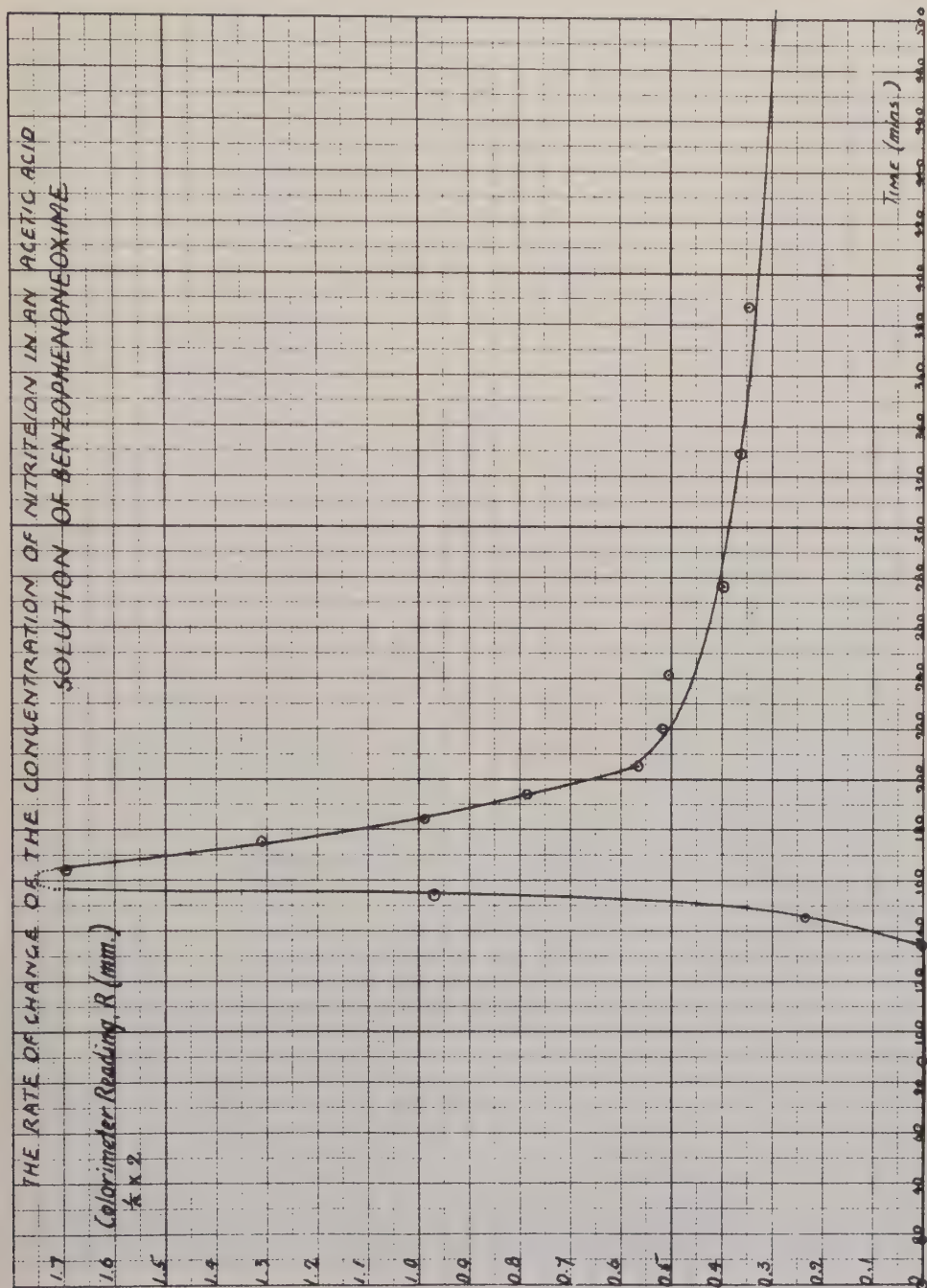
(ii)

Benzophenoneoxime: 0.3131 g. per 250.0 cc.
 Volume of samples: 9.99 cc. for oxime; 1 cc.
 for nitrite ion
 Concentration of permanganate: 0.01051 N
 Blank analysis: 0.45 cc.

Time (minutes)	Titration (cc.)	R Dial Reading on Color- imeter (mm.)	$\frac{1}{R} \times 10^*$
0	12.08 **	∞	0
8	12.46		
18		∞	0
42	12.26		
65		∞	0
81	12.47		
124	12.33		
136		∞	0
154	12.32		
176		∞	0
199		∞	0
227		∞	0
240		∞	0
253		∞	0
272		∞	0
298		∞	0
377		25.40	0.3938
379	11.29		
381		21.50	0.4651
384	10.47		
385		17.00	0.5883
388		15.00	0.6667
391	8.92		
395		9.5	1.053
399	6.17		
403		8.9	1.124
406	5.25		
412		8.2	1.220
416	5.11		
422		10.2	0.9804
427	5.27		
437		14.5	0.6896
446	4.99		
466		16.3	0.6135
492		22.2	0.4504
497	5.59		
1649	5.93		

* The factor 10 is for convenience in plotting.

** Calculated



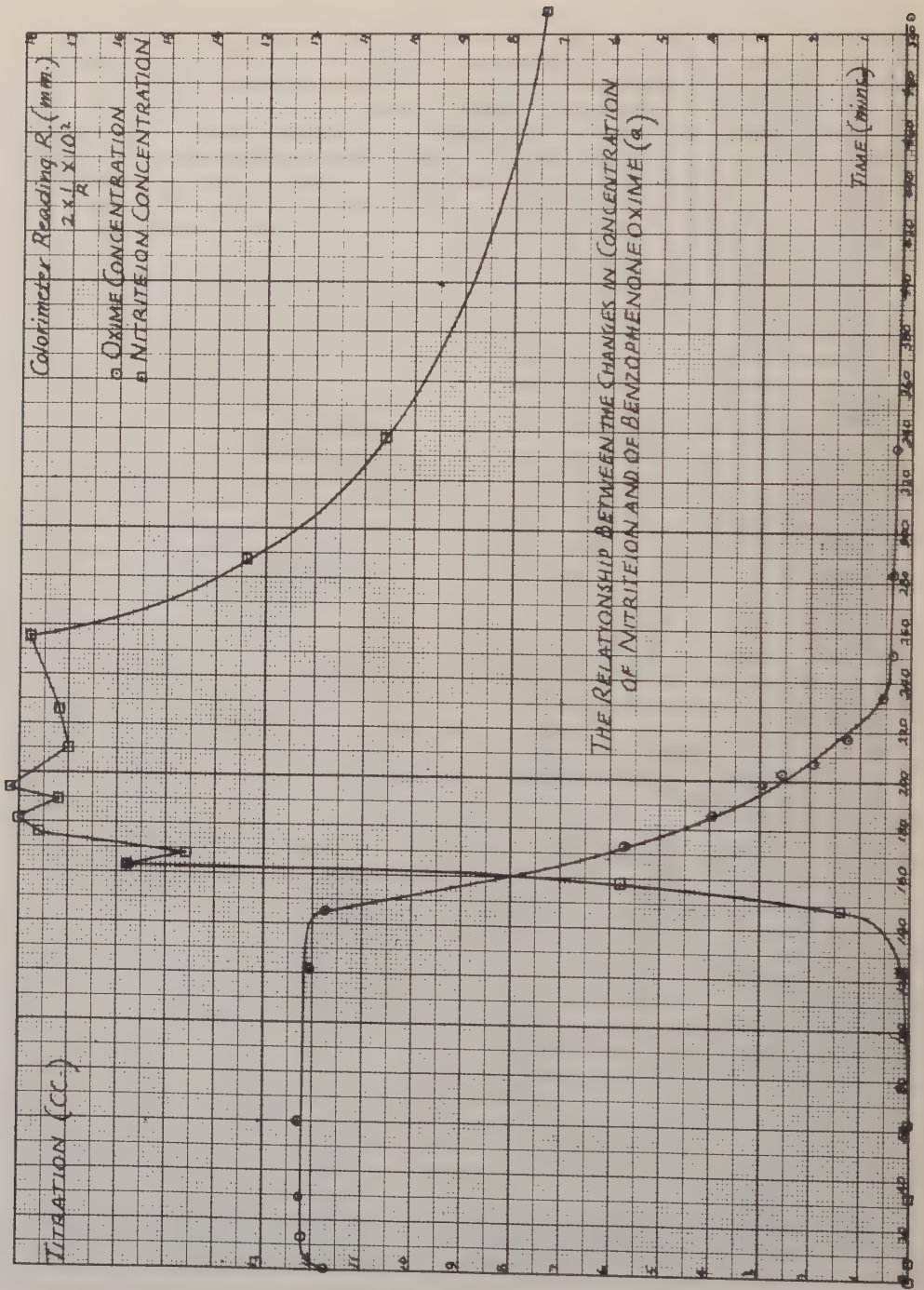


Fig. 11

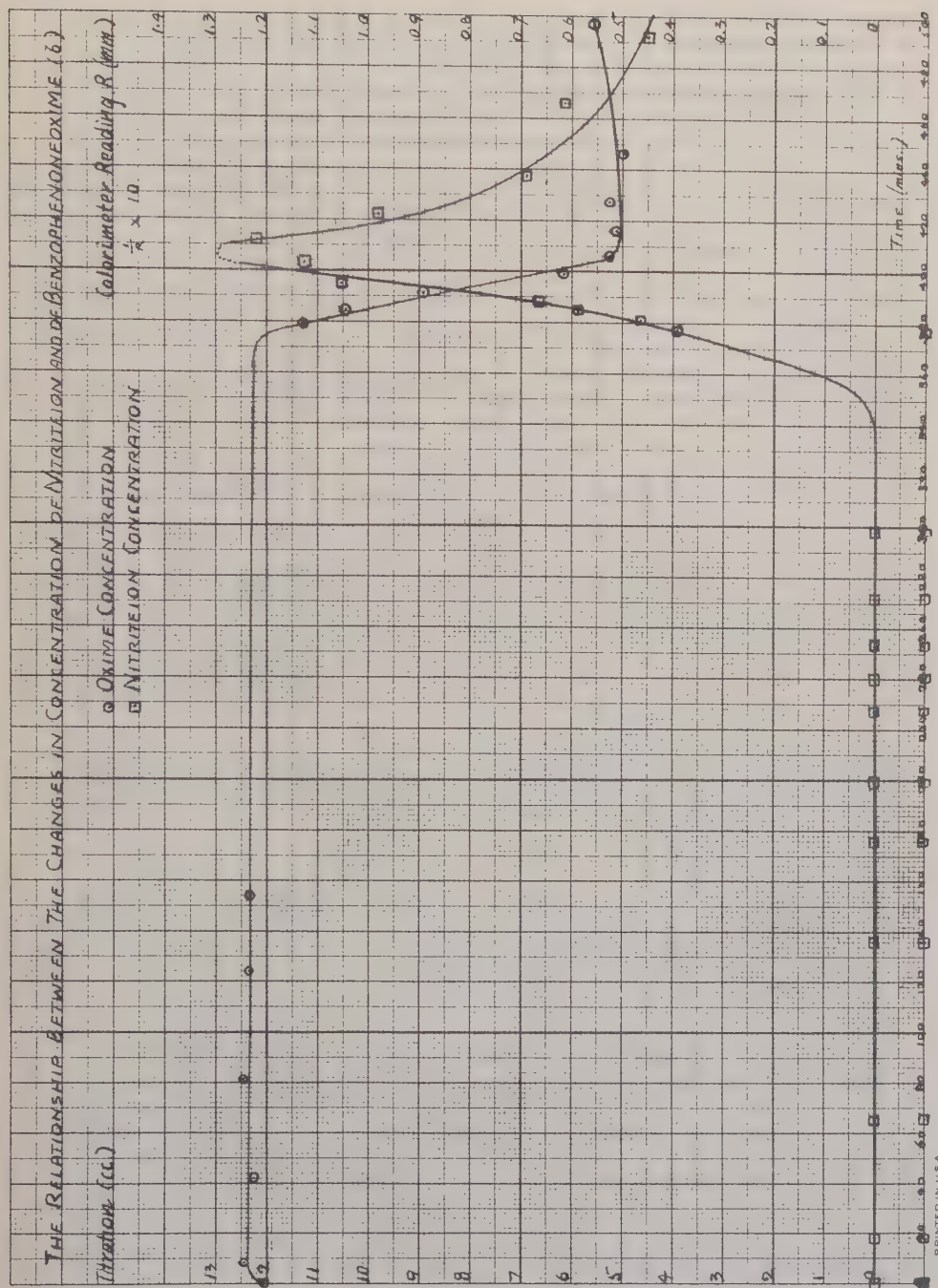


Fig. 12

Summary

(1) An improved method for the preparation of benzophenoneoxime has been described. The reaction is allowed to proceed at room temperature for two hours. The yield is theoretical, and no recrystallization of the product is necessary.

(2) A volumetric method for the determination of an oxime has been described. The oxime is oxidized by excess ferric sulphate in hot acidic solution, and the ferrous salt produced is determined by titration with potassium permanganate.

(3) Attention has been called to the effects on the analysis of hydroxylamine hydrochloride and of benzophenoneoxime, in the presence of acetic acid, of minute traces of impurities in the acid. An acetic acid of sufficient purity for all ordinary purposes may cause deviations in this analysis of three or four percent; and the ordinary methods of purification are not effective in removing the impurities. The synthetic acetic acid manufactured by the Niacet Chemicals Corporation is free from these undesirable features.

(4) Acetic acid of a high degree of purity was prepared, and the values of some of the physical constants for this acid have been measured and recorded.

(5) The accelerating effect of the oxides of nitrogen on the decomposition of benzophenoneoxime has been noted, and also the fact that in the absence of these oxides, the oxime may be stored indefinitely in an atmosphere of air, carbon dioxide, oxygen, nitric oxide, or nitrous oxide. An atmosphere of nitrous oxide is the most favourable for the preservation of the oxime.

(6) Where a delicate qualitative test for a substance is known, it has been indicated that it may be possible to employ the reaction involved in the test for the removal of traces of that substance from another.

(7) The autocatalytic decomposition of benzophenoneoxime in acetic acid solution has been observed, and its rate has been measured. After an induction period of about four hours, the oxime begins to decompose; the greater part of the transformation takes place rapidly, and after about half an hour the decomposition is practically complete.

(8) The catalytic effect of water, sodium nitrite, nitrous oxide, and acetanilide on this transformation of benzophenoneoxime has been measured. Water is the most important of all these, for in its absence the transformation does not occur. Acetanilide has no effect on the length of the induction period.

(9) The rates of change in the concentration of nitrite ion and of oxime, during the course of the transformation in acetic acid solution, have been measured. Traces of nitrite ion are found in the solution at the close of the induction period, and the amount rapidly increases and then diminishes more gradually. The concentration of the nitrite ion is at its maximum value at about the same time that the transformation of the oxime is occurring most rapidly.

(10) Two colour tests, indicating the termination of the induction period of the decomposition of benzophenoneoxime, have been described.

